

0.40 g of potassium persulfate

The afore-indicated components were mixed with one another homogeneously at room temperature (20-25 °C) or with gentle heating (35-40 °C). If necessary, the pH of the 5 ready-to-use colorant (A) was adjusted to the value given in Table 2 with sodium hydroxide solution, sodium carbonate, ammonia or citric acid.

The ready-to-use colorant was applied to bleached hair and uniformly distributed with a brush. After an exposure time of 30 minutes at 40° C, the hair was rinsed with lukewarm 10 water, washed with a commercial shampoo, rinsed with lukewarm water and then dried.

The amount of CH-active compound of formulas (II) to (IX) and the colorations obtained are collected in the following Table 2.

15

Table 2

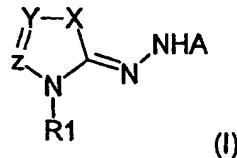
Example No.	CH-Active Compound Used, (Amount in g)	pH	Coloration
7	thiobarbituric acid (0.36 g)	9.3	copper shades
8	malonic acid dinitrile (0.17 g)	9.1	golden-yellow

Unless otherwise indicated, all percentages given in the present application are by 20 weight.

25

C L A I M S

1. Ready-to-use agent for coloring keratin fibers, characterized in that it contains (a) at least one hydrazone derivative of formula (I) or a physiologically compatible salt thereof



5 wherein

X stands for oxygen, sulfur or NR₂,

Y stands for C-R3 or nitrogen and

Z stands for C-R4 or nitrogen,

provided that the heterocyclic part of the compound of formula (I) contains at the most
10 three heteroatoms;

A stands for hydrogen, an acetyl group, a trifluoroacetyl group, a formyl group, a (C₁-C₆)-alkylsulfonyl group or an arylsulfonyl group;

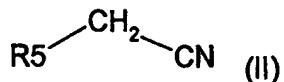
R1 and **R2** can be equal or different and independently of each other denote a saturated or unsaturated (C_1 - C_{12})-alkyl group, a halogen-substituted (C_1 - C_{12})-alkyl group, a hydroxy- (C_1 - C_{12})-alkyl group, an amino- (C_1 - C_{12})-alkyl group, a sulfonic acid- (C_1 - C_{12})-alkyl group, a formyl group, a $-C(O)-(C_1-C_{12})$ -alkyl group, a substituted or unsubstituted $-C(O)$ -phenyl group, a $-C(O)NH-(C_1-C_{12})$ -alkyl group, a substituted or unsubstituted $-C(O)NH$ -phenyl group, a substituted or unsubstituted phenyl group or a benzyl group;

20 **R3** and **R4** can be identical or different and independently of each other denote hydrogen, a halogen atom, a saturated or unsaturated (C_1 - C_{12})-alkyl group, a halogen-substituted (C_1 - C_{12})-alkyl group, a hydroxyl group, a hydroxy- $(C_1$ - C_{12})-alkyl group, a (C_1 - C_{12})-alkoxy group, a cyano group, a nitro group, an amino group, a (C_1 - C_{12})-alkylamino group, a di(C_1 - C_{12})-alkylamino group, a carboxyl group, a $-C(O)O-(C_1$ - C_{12})-alkyl group, a substituted or unsubstituted $-C(O)O$ -phenyl group, a substituted or unsubstituted phenyl group or a
25 naphthyl group:

and when **Y** and **Z** stand for C-R3 and C-R4, **R3** and **R4** together with the remainder of the molecule can form a heterocyclic or carbocyclic, saturated or unsaturated, substituted

or unsubstituted ring system;

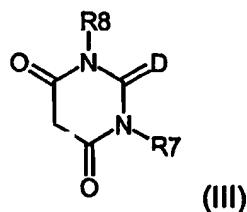
(b) at least one CH-active compound of formulas (II) to (IX) with



wherein **R5** denotes a cyano group, a (CO)-R6 carbonyl function, with **R6** standing for a

5 (C₁-C₁₂)-alkoxy group, an amino group, a (C₁-C₁₂)-alkylamino group, a (C₁-C₁₂)-alkyl group or an aryl

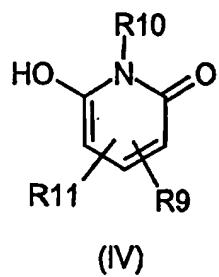
group;



10

wherein **R7** and **R8** can be equal or different and denote hydrogen, a (C₁-C₁₂)-alkyl group, a monohydroxy-(C₁-C₁₂)-alkyl group, a polyhydroxy-(C₂-C₁₂)-alkyl group, a mono-(C₁-C₆)-alkoxy-(C₁-C₆)-alkyl group, a poly-(C₁-C₆)-alkoxy-(C₂-C₆)-alkyl group, an amino-(C₁-C₁₂)-alkyl group, or a carbocyclic or heterocyclic, substituted or unsubstituted aromatic compound,

15 and **D** stands for a sulfur atom or oxygen atom;



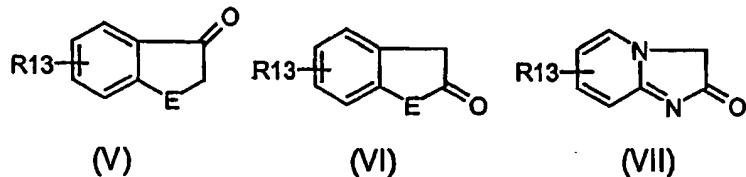
wherein **R9** denotes a hydrogen atom, a nitrile group, a (C₁-C₁₂)-alkyl group, a carbocyclic or heterocyclic aromatic compound or a (CO)-R12 carbonyl function, with **R12** standing

20 for hydrogen, a hydroxyl group, a (C₁-C₁₂)-alkoxy group, an amino group, a (C₁-C₁₂)-

alkylamino group, a (C₁-C₁₂)-alkyl group or an aryl group, and

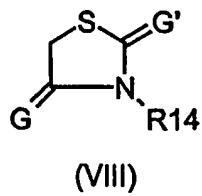
R10 and **R11** can be equal or different and independently of each other denote hydrogen, a (C₁-C₁₂)-alkyl group, a monohydroxy-(C₁-C₁₂)-alkyl group, a polyhydroxy-(C₂-C₁₂)-alkyl group, a mono-(C₁-C₆)-alkoxy-(C₁-C₆)-alkyl group, a poly-(C₁-C₆)-alkoxy-(C₂-C₆)-alkyl

5 group, an amino- (C_1-C_{12}) -alkyl group, or a carbocyclic or heterocyclic aromatic compound;



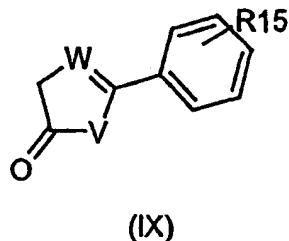
wherein **E** denotes an oxygen atom, a sulfur atom of an NR' amino group, with R' standing for hydrogen or a substituted or unsubstituted (C₁-C₁₂)-alkyl group, and

R13 stands for a hydrogen atom, a halogen atom, a hydroxyl group, a cyano group, a nitro group, a (C₁-C₁₂)-alkyl group, a monohydroxy-(C₁-C₁₂)-alkyl group, a polyhydroxy-(C₂-C₁₂)-alkyl group, a mono-(C₁-C₆)-alkoxy-(C₁-C₆)-alkyl group, a poly-(C₁-C₆)-alkoxy-(C₁-C₆)-alkyl group, an amino-(C₁-C₁₂)-alkyl group, or a carbocyclic or heterocyclic aromatic compound, a carboxamide or a sulfonamide;



wherein **G** and **G'** can be equal or different and independently of each other denote an oxygen atom, sulfur atom or an NR'' amino group, with R'' standing for hydrogen or a substituted or un-substituted (C_1 - C_{12})-alkyl group, and

20 **R14** denotes hydrogen, a substituted or unsubstituted (C_1 - C_{12})-alkyl group or a carbocyclic or heterocyclic, substituted or unsubstituted aromatic compound;



wherein **V** stands for an oxygen atom or an NR'' amino group, with R'' denoting hydrogen or a substituted or unsubstituted- (C_1-C_{12}) -alkyl group and

5 **R15** stands for a hydrogen atom, a halogen atom, a hydroxyl group, a cyano group, a nitro group, a (C_1-C_{12}) -alkyl group, a monohydroxy- (C_1-C_{12}) -alkyl group, a polyhydroxy- (C_2-C_{12}) -alkyl group, a mono- (C_1-C_6) -alkoxy- (C_1-C_6) -alkyl group, a poly- (C_1-C_6) -alkoxy- (C_1-C_6) -alkyl group, an amino- (C_1-C_{12}) -alkyl group, a carbocyclic or heterocyclic aromatic compound, a carboxamide or a sulfonamide; and

10 (c) at least one oxidant.

2. Agent as defined in claim 1, characterized in that in formula (I) **X** stands for sulfur, **Y** stands for $C-R3$, **Z** stands for $C-R4$ and **A** denotes hydrogen.

15 3. Agent as defined in claim 1 or 2, characterized in that the hydrazone derivative of formula (I) is selected from among
 3-methyl-2(3H)thiazolone hydrazone,
 3,4-dimethyl-2(3H)thiazolone hydrazone,
 4-tert.butyl-3-methyl-2(3H)thiazolone hydrazone,
 20 3-methyl-4-phenyl-2(3H)thiazolone hydrazone,
 3-methyl-4-(4-tolyl)-2(3H)-thiazolone hydrazone,
 4-(4-methoxy)phenyl-3-methyl-2(3H)-thiazolone hydrazone,
 4-(4-ethoxy)phenyl-3-methyl-2(3H)-thiazolone hydrazone,
 4-(4-bromophenyl)-3-methyl-2(3H)-thiazolone hydrazone,
 25 4-(3-bromophenyl)-3-methyl-2(3H)-thiazolone hydrazone,
 4-(4-chlorophenyl)-3-methyl-2(3H)-thiazolone hydrazone,

4-(3-chlorophenyl)-3-methyl-2(3H)-thiazolone hydrazone,
3-methyl-4-(4-nitrophenyl)-2(3H)-thiazolone hydrazone,
3-methyl-4-(3-nitrophenyl)-2(3H)-thiazolone hydrazone,
4-[(1,1'-biphenyl)-4-yl]-3-methyl-2(3H)-thiazolone hydrazone,
5 ethyl 2-hydrazone-2,3-dihydro-3-methyl-4-thiazolecarboxylate,
3,4,5-trimethyl-2(3H)-thiazolone hydrazone,
3,4-dimethyl-5-phenyl-2(3H)-thiazolone hydrazone,
3,5-dimethyl-4-phenyl-2(3H)-thiazolone hydrazone,
4,5-diphenyl-3-methyl-2(3H)-thiazolone hydrazone,
10 5-ethyl-3-methyl-4-phenyl-2(3H)-thiazolone hydrazone,
4-(4-bromophenyl)-3-methyl-5-phenyl-2(3H)-thiazolone hydrazone,
3-methyl-5-phenyl-4-(4-tolyl)-2(3H)-thiazolone hydrazone,
5-(4-chlorophenyl)-4-phenyl-3-methyl-2(3H)-thiazolone hydrazone,
5-(4-chlorophenyl)-4-(4-methoxyphenyl)-3-methyl-2(3H)-thiazolone hydrazone,
15 ethyl 2-hydrazone-2,3-dihydro-3,4-dimethyl-4-thiazolecarboxylate,
4-amino-2-hydrazone-2,3-dihydro-3-methyl-5-thiazole carbonitrile
4,5-dimethyl-3-ethyl-2(3H)-thiazolone hydrazone,
ethyl 2-hydrazone-2,3-dihydro-3-ethyl-4-methylthiazolecarboxylate,
5-methyl-3-(1-methylethyl)-4-phenyl-2(3H)-thiazolone hydrazone,
20 4,5-diphenyl-3-(1-methylethyl)-2(3H)-thiazolone hydrazone
4,5-diphenyl-3-propyl-2(3H)-thiazolone hydrazone,
3-butyl-4,5-diphenyl-2(3H)-thiazolone hydrazone,
4,5-diphenyl-3-(2-methylpropyl)-2(3H)-thiazolone hydrazone,
3-(2-propenyl)-2(3H)-thiazolone hydrazone,
25 4-methyl-3-(2-propenyl)-2(3H)-thiazolone hydrazone,
4-tert.butyl-3-(2-propenyl)-2(3H)-thiazolone hydrazone,
4-phenyl-3-(2-propenyl)-2(3H)-thiazolone hydrazone,
4,5-diphenyl-3-(2-propenyl)-2(3H)-thiazolone hydrazone,
3-hydroxyethyl-2(3H)-thiazolone hydrazone,
30 3-hydroxyethyl-4-methyl-2(3H)-thiazolone hydrazone,

3-aminoethyl-2(3H)-thiazolone hydrazone,
3-aminoethyl-4-methyl-2(3H)-thiazolone hydrazone,
3-phenyl-2(3H)-thiazolone hydrazone,
4-methyl-3-phenyl-2(3H)-thiazolone hydrazone,
5 3,4-diphenyl-2(3H)-thiazolone hydrazone,
4-p-biphenyl-3-phenyl-2(3H)-thiazolone hydrazone,
4-(4-methoxy)phenyl-3-phenyl-2(3H)-thiazolone hydrazone,
4-tert.butyl-3-phenyl-2(3H)-thiazolone hydrazone,
3,4-diphenyl-5-methyl-2(3H)-thiazolone hydrazone,
10 3,4,5-triphenyl-2(3H)-thiazolone hydrazone,
4,5-dimethyl-3-(phenylmethyl)-2(3H)-thiazolone hydrazone,
ethyl 2-hydrazone-2,3-dihydro-3-[(phenylamino)carbonyl]-4-methylthiazolecarboxylate
3-methyl-4,5,6,7-tetrahydro-2(3H)-benzothiazolone hydrazone,
3-methyl-2(3H)benzothiazolone hydrazone,
15 3,6-dimethyl-2(3H)benzothiazolone hydrazone,
6-chloro-3-methyl-2(3H)benzothiazolone hydrazone,
7-chloro-3-methyl-2(3H)benzothiazolone hydrazone,
6-hydroxy-3-methyl-2(3H)benzothiazolone hydrazone,
5-methoxy-3-methyl-2(3H)benzothiazolone hydrazone,
20 7-methoxy-3-methyl-2(3H)benzothiazolone hydrazone,
5,6-dimethoxy-3-methyl-2(3H)benzothiazolone hydrazone,
5-ethoxy-3-methyl-2(3H)benzothiazolone hydrazone,
6-ethoxy-3-methyl-2(3H)benzothiazolone hydrazone,
3-methyl-5-nitro-2(3H)benzothiazolone hydrazone,
25 3-methyl-6-nitro-2(3H)benzothiazolone hydrazone,
5-acetamido-3-methyl-2(3H)benzothiazolone hydrazone,
6-acetamido-3-methyl-2(3H)benzothiazolone hydrazone,
5-anilino-3-methyl-2(3H)benzothiazolone hydrazone,
6-anilino-3-methyl-2(3H)benzothiazolone hydrazone,
30 2-hydrazone-2,3-dihydro-3-methyl-6-benzothiazolecarboxylic acid,

2-hydrazone-2,3-dihydro-3-methyl-4-benzothiazolesulfonic acid,
2-hydrazone-2,3-dihydro-3-methyl-5-benzothiazolesulfonic acid,
2-hydrazone-2,3-dihydro-3-methyl-6-benzothiazolesulfonic acid,
2-hydrazone-2,3-dihydro-3-methyl-7-benzothiazolesulfonic acid,
5 2-hydrazone-2,3-dihydro-N,N,3-trimethyl-6-benzothiazolesulfonamide,
[(2-hydrazone-2,3-dihydro-3-methyl-6-benzothiazolyl)oxy]acetic acid hydrazide,
3-methylnaphtho[2,3-d]thiazol-2(3H)one hydrazone
3-ethyl-2(3H)benzothiazolone hydrazone,
6-ethoxy-3-ethyl-2(3H)benzothiazolone hydrazone,
10 3-propyl-2(3H)benzothiazolone hydrazone,
3-butyl-2(3H)benzothiazolone hydrazone,
3-hexyl-2(3H)benzothiazolone hydrazone,
3-hydroxyethyl-2(3H)benzothiazolone hydrazone,
3-aminoethyl-2(3H)benzothiazolone hydrazone,
15 3-p-methylbenzyl-2(3H)benzothiazolone hydrazone,
2-hydrazone -2,3-dihydro-3-(2-hydroxyethyl)-6-benzothiazolecarboxylic acid
2-hydrazone -2,3-dihydro-6-methoxy-3(2H)benzothiazolepropanesulfonic acid,
6-hexadecyloxy-2-hydrazone-3(2H)benzothiazolepropanesulfonic acid,
ethyl 2-keto-3-benzothiazolineacetate hydrazone,
20 3-acetyl-2(3H)benzothiazolone hydrazone and 2-hydrazone-3(2H)
benzothiazole carboxaldehyde.

4. Agent as defined in one of claims 1 to 3, characterized in that the active CH-active
com-pound is selected from among cyanoacetic acid, methyl cyanoacetate, ethyl
25 cyanoacetate, malonic acid dinitrile, pivaloylacetone, 2-cyanoacetamide, 2-cyano-1-
methyl-4-nitrobenzene, barbituric acid, thiobarbituric acid, 1,3-dimethylthiobarbituric acid,
1-methyl-1,2-dihydro-6-hydroxy-4-methyl-2-ketopyridine-3-carbonitrile,
1-ethyl,1,2-dihydro-6-hydroxy-4-methyl-2-ketopyridine-3-carbonitrile, 1-hydroxyethyl-1,2-
dihydro-6-hydroxy-4-methyl-2-ketopyridine-3-carbonitrile, 1,3-dihydro-2H-indol-
30 2-one, benzofuran-3(2H)-one, 2-phenyl-3,5-dihydroimidazol-4-one, 3-indoxyl acetate, 2-

thioxo-4-thiazolidinone and 4-keto-2-thioxo-3-thiazolidinylacetic acid.

5. Agent as defined in claims 1 to 4, characterized in that the oxidant is selected from among hydrogen peroxide or an addition compound thereof, persalts, peracids and enzymatic oxidation systems.
6. Agent as defined in claim 5, characterized in that the oxidant is selected from among hydrogen peroxide and an addition product thereof and persulfate salts.
- 10 7. Agent as defined in one of claims 1 to 6, characterized in that it contains the hydrazone derivatives of formula (I) and the CH-active compound of formulas (II) to (IX) and the oxidant in a total amount from 0.01 to 10 weight percent each.
- 15 8. Agent as defined in one of claims 1 to 7, characterized in that it contains additionally from 0.01 to 10 weight percent of a physiologically unobjectionable direct dye from the group of cationic and anionic dyes, disperse dyes, nitro dyes, azo dyes, quinone dyes and triphenylmethane dyes.
- 20 9. Agent as defined in one of claims 1 to 8, characterized in that it has a pH from 7 to 11.
10. Agent as defined in one of claims 1 to 9, characterized in that it is a hair colorant.
- 25 11. Two-component kit consisting of a dye carrier composition (A1) containing the compound of formula (I) and another dye carrier composition (A2) containing the CH-active compound of formulas (II) to (IX) and an oxidant.
12. Three-component kit consisting of a dye carrier composition (A1) containing the compound of formula (I), another dye carrier composition (A2) containing the CH-active compound of formulas (II) to (IX) and an oxidant, and a third component (A3) containing

compound of formulas (II) to (IX) and an oxidant, and a third component (A3) containing an agent for pH adjustment.

13. Two-component kit consisting of a powdered dye carrier composition (A1) containing the compounds of formula (I), the CH-active compound of formulas (II) to (IX)

5 and an oxidant as well as optionally other common powdered cosmetic additives, and a liquid cosmetic composition (A2).

14. Three-component kit consisting of a dye carrier composition (A1) containing the com-pounds of formula (I), another dye carrier composition (A2) containing the CH-active

10 compound of formulas (II) to (IX) and an oxidant-containing third component (A3).

15. Method for coloring hair whereby a colorant as defined in one of claims 1 to 10 is applied to the hair, and after an exposure time of 5 to 60 minutes at a temperature from

20 to 50 °C the hair is rinsed with water, optionally washed with a shampoo and then

15 dried.

20

25

30

31